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WATER SOLUBLE POLYESTER ADHESIVE
[Suiyosei poriesuterukei secchakuzai]

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1. Name of this Invention

WATER-SOLUBLE POLYESTER ADHESIVE

2. Claim(s)

[1] Water-soluble polyester adhesive, a polyester copolymer, comprising (1) dicarboxylic acid (and/or its ester-forming derivative) consisting of an aromatic dicarboxylic acid component and saturated straight-chain aliphatic dicarboxylic acid component having 4 - 8 methylene groups at the mol ratio of 10/1 - 10/7.5 and (2) glycol; wherein the composition ratio satisfies:

(A) The ratio of ester-forming sulfonic acid alkali metallic salt to the total acid amount is 5.5 - 7.5 mol%,

(B) The ratio of diethylene glycol to the total amount of glycol component is 50 - 100 mol%, and
the ratio of phosphorus amount in the phosphorus compound to the polyester is 20 - 1000 ppm.

[2] Water-soluble polyester adhesive according to Claim 1, wherein the aromatic dicarboxylic acid component is terephthalic acid/isophthalic acid existing in the mol ratio of 8/2 - 2/8.

[3] Water-soluble polyester adhesive according to Claim 1, wherein the saturated straight-chain aliphatic dicarboxylic acid component is Adipic acid.

* Numbers in the margin indicate pagination in the foreign text.

[4] Water-soluble polyester adhesive according to Claim 1, wherein the ester-forming sulfonic acid alkali metallic salt compound is 5-sodium sulfo isophthalic acid.

[5] Water-soluble polyester adhesive according to Claim 1, wherein (1) the aromatic dicarboxylic acid component consists of terephthalic acid and isophthalic acid; (2) the saturated straight-chain aliphatic dicarboxylic component is adipic acid; and (3) ester-forming sulfonic acid alkali metallic salt compound is 5-sodium sulfo isophthalic acid.

[6] Water-soluble polyester adhesive according to Claim 1, wherein the amount of diethylene glycol in the glycol component is 40 - 80 mol%.

[7] Water-soluble polyester adhesive according to Claim 1, wherein the phosphoric compound is phosphoric acid or phosphoric acid ester.

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3. Detailed Explanation of this Invention

[Industrial Field]

This invention pertains to a water-soluble polyester type adhesive and is particularly associated with a water-soluble polyester type adhesive agent providing (1) excellent adhesive property for a polyester film and metallic foil, various plastics, particularly gelatin, polyvinyl alcohol, etc., and (2) capacity of improving the work environment problem. Linear polyester film, particularly polyethylene terephthalate biaxial extension film having

excellent characteristics, such as transparency, measurement stability, durability, etc., is widely utilized in the fields of photographic sensitizer, metallic vapor deposition base, drafting base, magnetic tape base, packaging material, etc. In this case, the polyester film is rarely used as a single element. For example, the film requires an adhesive agent for adhering to a gelatin layer when used as a photographic base, to a magnetic layer when used as a magnetic tape base, and to a mat-forming agent layer when used as a drafting base. However, generally speaking, the adhesive agent having affinity with the polyester film surface has low adhesive strength to the surface layer. On the other hand, the adhesive agent having an affinity with the surface layer has low adhesive strength with the polyester film surface.

In order to improve the adhesiveness between the linear polyester and metallic foil, various plastic, gelatin (particularly), polyvinyl alcohol, etc., an adhesive agent soluble in an organic solvent is commonly used. However, in recent years, restrictions are placed on the use of these materials for assuring the safety of work environment.

The purpose of this invention is to provide a polyester type adhesive agent which is water-soluble and has excellent adhesiveness so as to solve the abovementioned problems.

Examples of the conventionally known polyesters having the adhesiveness are:

(1) Polyester prepared by copolymerizing polyester and 40 - 80 wt% of polyalkylene ether (US Patent No. 3,023,192, etc.)

(2) Polyester prepared by copolymerizing polyethylene terephthalate with isophthalic acid, tetrahydroterephthalic acid, aliphatic dicarboxylic acid, etc. (US Patent No. 2,829,747, Britain Patent No. 861, 835, etc.)

(3) Polyester prepared by copolymerizing polyester with at least 20 mol% of polyethylene glycol having the polymerization ratio of 2 - 10 and at least about 8 mol% of sulfonic acid metallic salt compound (Japan Patent No. 47-40875, etc.)

(4) Polyester prepared by copolymerizing polyester with aliphatic dicarboxylic acid and diethylene glycol (Japan Patent No. 51-48197).

However, the polyester elastic bodies (1), (2), and (4) described above are soluble in an organic solvent but completely insoluble in water. Therefore, when used as an adhesive agent, the agent must be prepared as a hot-melt type or agent dissolved in an organic solvent which would cause the problem in the work environment.

On the other hand, the agent (3) associated with the polyester having water-solubility and adhesiveness is extremely low in water-resistance.

Hence, the developers of this invention thoroughly investigated the water-soluble polyester adhesive agent which could solve the

problems of the conventional polyester type adhesive agents and working environment problems and have completed this invention.

That is, this invention provides a water-soluble polyester adhesive, a polyester copolymer, comprising (1) dicarboxylic acid (and/or its ester-forming derivative) consisting of an aromatic dicarboxylic acid component and saturated straight-chain aliphatic dicarboxylic acid component having 4 - 8 methylene groups at the mol ratio of 10/1 - 10/7.5 and (2) glycol; wherein the composition ratio satisfies:

- (A) The ratio of ester-forming sulfonic acid alkali metallic salt to the total acid amount is 3.5 - 7.5 mol%,
- (B) The ratio of diethylene glycol to the total amount of glycol component is 30 - 100 mol%, and

the ratio of phosphorus amount in the phosphorus compound to the polyester is 20 - 1000 ppm.

Examples of aromatic dicarboxylic acid component used in this invention are terephthalic acid, isophthalic acid, phthalic acid, 2,5-dimethyl terephthalic acid, 2,6-naphthalene dicarboxylic acid, 1,4-naphthalene dicarboxylic acid, 2,5-naphthalene dicarboxylic acid, biphenyl dicarboxylic acid, and ester-forming derivatives of these materials, where the combination of terephthalic acid (or its ester-forming derivative) and isophthalic acid (or its ester-forming derivative) is preferred. In this case, when the mol ratio is 8/2 -

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2/8, particularly preferable results can be provided to the coating property of the polyester base material and solubility in water.

The saturated straight-chain aliphatic dicarboxylic acid having 4 - 8 methylene groups is at least one material selected from adipic acid, pymeric acid, spelic acid, azalaic acid, sebacic acid, and ester-forming derivatives of these materials. If the saturated straight-chain aliphatic dicarboxylic acid has 3 or less methylene groups, strong adhesiveness is completely unattainable. On the other hand, if it has 9 or more methylene groups, the adhesive strength worsens with the passage of time.

Moreover, as the mol ratio as the total acid component, the mol ratio of aromatic dicarboxylic acid component and saturated straight-chain aliphatic dicarboxylic acid should be 10/1 - 10/7.5 for providing excellent adhesiveness between the polyester base material and gelatin, polyolefin, and polyvinyl alcohol type resins. If the mol ratio of the saturated straight-chain aliphatic dicarboxylic acid is less than 1 when the aromatic dicarboxylic acid component ratio is 10, water solubility, uniform coating property, and adhesiveness become insufficient. On the other hand, if the ratio exceeds 7.5, the water-resistance becomes insufficient.

In addition, by copolymerizing an ester-forming sulfonic acid alkali metallic salt with the abovementioned composition, the water-solubility can be accelerated, while the adhesiveness effect can be increased.

Examples of ester-forming sulfonic acid alkali metallic salt are alkali metallic salts, such as sulfoterephthalic acid, 5-sulfoisophthalic acid, 4-sulfoisophthalic acid, 4-sulfohaphthalene-2,7-dicarboxylic acid, sulfo-p-xylylene glycol-2-sulfo-1,4-bis(hydroxyl ethoxy) benzene, etc. and the ester-forming derivatives of these materials, where 5-sulfoisophthalic acid, salt or potassium salt of sulfoterephthalic acid are preferred.

However, if the metallic salt of sulfonate compound is other than the alkali metal, the water-solubility of the created polymer deteriorates, thereby subsequently failing to achieve the purpose of this invention.

When the amount of abovementioned ester-forming sulfonic acid alkali metallic salt is 3.5 - 7.5 mol% to the total acid component, the effectiveness of this invention can be manifested.

The amount less than 3.5 mol% drastically worsens the water-solubility of the created polymer and stability of an aqueous solution. On the other hand, an amount exceeding 7.5 mol% is not recommended as it reduces the water-resistance of the adhesive layer when practically applied, and therefore. The diethylene glycol used in this invention provides adequate elasticity at room temperature and produces an assisting effect for making the agent water-soluble. The amount of 30 mol% - 100 mol%, preferably 40 - 80 mol% of this material can provide the greatest effectiveness.

However, if the amount is less than 30 mol%, the impact peeling resistance worsens.

Examples of glycol substances other than diethylene glycol are ethylene glycol, 1,2-propane diol, 1,5-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, 1,8-octane diol, 1,3-cyclohexane dimethanol, 1,2-cyclohexane dimethanol, 1,4-cyclohexane dimethanol, etc., where ethylene glycol, 1,3-propane diol, 1,4-buthane diol, etc. are preferred.

As the amount of phosphorus compound included in the obtained polyester copolymer, the phosphorus quantity should be 20 - 1000 ppm, preferably 40 - 800 ppm.

If the amount is less than 20 ppm, water-resistance will be insufficient, subsequently causing the particularly serious drawback of worsening adhesiveness to polyvinyl alcohol with the passage of time.

On the other hand, an amount exceeding 1000 ppm damages the adequate elasticity of the polyester copolymer and worsens the water-resistance. As a result, the aimed properties cannot be obtained. /274

Examples of phosphorus compounds are phosphoric acid, phosphorous acid, phosphonic acid, phosphinic acid (and/or its ester compound), phosphonium salt compound, phosphoric acid boron, pyrrolic acid, phosphoric acid triamide, phosphoric acid ammonium, etc. The timing of adding phosphoric compounds may be arbitrarily selected before or after the ester-exchange reaction. To produce the polyester

copolymer which is the adhesive agent of this invention, the method of producing polyethylene terephthalate can be used.

Examples of production methods are:

(1) A specific amount of dicarboxylic acid dimethyl ester and glycol are heated at 140 - 240°C in the presence of regular ester-exchange catalyst consisting of 1 water salt of calcium acetate, 4 water salts of manganese acetate, 4 water salts of magnesium acetate, 2 water salts of zinc acetate, etc., and the ester-exchange reaction is performed while removing the created methanol. Then, after glycol is removed from the material, the material is condensation polymerized under high temperature vacuumed atmosphere (at 200 - 290°C under 0.01 - 50 mmHg) under the presence of a polymerization catalyst (typical examples of triantimony oxide, germanium dioxide, tetrabutyl titanate, etc.), and a phosphoric compound, such as phosphorus acid, phosphoric acid (and/or its esterified substance), etc.

(2) Dicarboxylic acid and glycol are esterified at 150 - 250°C under normal or increased pressure while created water is removed. Then, the material is condensation polymerized under the presence of phosphoric compound and condensation polymerization catalyst.

Moreover, if the ester-forming sulfonic acid alkali metallic salt compound is a carboxylic acid ethylene glycol ester or oxy compound, the phosphorus compound should be added before or after the

esterification; however, if it is dicarboxylic dimethyl ester, the phosphoric compound is preferably added prior to esterification.

In addition, if the aromatic dicarboxylic acid component, and if the saturated straight-chain aliphatic dicarboxylic acid component is aliphatic dicarboxylic acid, after the former is subjected to a regular ester-exchange, the latter substance is esterified to complete the condensation polymerization.

Various additives may be added to the obtained copolymer polyester. Examples are an anti-oxidization agent (e.g., hindered phenol) for improving the heat resistance, inorganic fine particles for improving the smoothness, organic lubricant and pigment, dye, water-soluble and water-dispersible polymer other than the copolymer polyester of this invention.

The specific viscosity (measured in O-chlorophenol at 25°C) of the water-soluble copolymer polyester of this invention is not particularly limited. However, if it is less than 0.3, sufficient adhesive strength cannot be produced. Therefore, the value should be 0.3 or higher. In addition, this copolymer polyester adhesive agent can be used as an aqueous solution. In this case, this aqueous solution does not need to be strictly based on the physical chemistry requirement, as a solution can consist of mostly dissolved materials with a part of finely dispersed substances.

The water-soluble copolymer polyester type adhesive agent has the following characteristics compared with the conventional polyester adhesive agents:

- (A) Since it does not use an organic solvent, consideration on the work-environmental safety (e.g., toxicity, ignition property, etc.) can be drastically simplified.
- (B) The agent which is an aqueous solution can be widely utilized in the areas where the hot-melt type adhesive agent cannot be applied. Therefore, the adhesive agent can be used extremely effectively as a sizing agent for fabric production process and coating agent for fiber and film.
- (C) The agent can be effectively used for heat-adhesion. For example, after the aqueous solution of this adhesive agent is coated to the base material, water is evaporated to form a polyester copolymer adhesive film. Then, the surface can be adhered by providing heat and pressure.
- (D) The adhesive agent is particularly effective for adhering a polyester film to polyvinyl alcohol, gelatin, and polyolefin.

Hereafter, this invention is explained further in detail based on the operational and comparison examples.

The following methods were used to evaluate obtained copolymerized polyesters.

(1) Water solubility

50 g of copolymerized polyester dissolved at 210°C under the nitrogen atmosphere copolymer were put in 1 liter of 95°C hot water and dissolved. The tank for dissolving the polyester was equipped with a stirrer and reflux device, allowing the polyester to be dissolved over 40 minutes under gradual stirring. Then, after the aqueous solution was gradually cooled to room temperature, the appearance was rated. /275

(2) Polyester film adhesiveness

The aqueous solution obtained in (1) was coated over a 50 μ thick biaxially extended polyethylene terephthalate film, and the moisture was evaporated. Then, a non-coated polyethylene terephthalate film was adhered to this coated film at 140°C with an electric iron.

The adhesion strength was examined by peeling off the layers in the direction of 180° and rated in 5 grades:

- 1: Complete absence of adhesion.
- 2: The films were adhered weakly and separated from the adhesion layer.
- 3: Although adhered strongly, the films peeled from the adhesive layer.
- 4: The films were strongly adhered, causing a partial layered peeling.

5: The films were extremely strongly adhered, causing tearing of the films.

(3) Adhesiveness to polyvinyl alcohol

The same aqueous solution was coated over a 50 μ thick biaxially extended polyethylene terephthalate film and dried at 180°C hot plate for 2 minutes, over which a 4% polyvinyl alcohol aqueous solution (saponification ratio = 99%) was coated and dried at 120°C for 3 minutes.

The obtained laminated film was left untouched in the atmosphere of 40°C and 65% RH for 24 hours and 1 month. Then, a 24 mm wide adhesive tape (Nichiban) was adhered to the polyvinyl alcohol surface and peeled in the direction of 180°. The result was rated in 5 grades:

- 1: Extremely weak adhesiveness. The film was completely peeled by the adhesive tape.
- 2: At least 50% of the film was peeled with the adhesive tape.
- 3: About 10 - 50% of the film was peeled with the adhesive tape.
- 4: Films were strongly adhered, limiting the peeling to less than 10%.
- 5: Films were extremely strongly adhered and absolutely unpeelable.

(4) Adhesiveness to gelatin

The same method as described in (3) was used.

(5) Water-resistance

The same aqueous solution was coated over a 50 μ thick biaxially extended polyethylene terephthalate film and dried at 180°C hot plate for 2 minutes. Then, two films were adhered using the adhesive surfaces and sealed at 140°C using an electric iron.

The prepared films were processed in 85°C hot water for 30 minutes. The adhesion strengths before and after the hot water process were compared and rated using a 5-grades rating system:

The hot-water treated strength compared with the untreated strength was:

- 1: Less than 50% of strength
- 2: About 70 - 50%
- 3: About 90 - 70%
- 4: About 95 - 90%
- 5: About 95% or higher

(6) Property of uniform coating

The aqueous solution was coated over the biaxially extended polyethylene terephthalate film using a photogravure roller and the condition was examined.

Operational example 1:

36.9 wt parts of terephthalic acid dimethyl, 30.4 wt parts of isophthalic acid dimethyl, 9.8 wt parts of 5-sodium sulfo isophthalic acid dimethyl ester, 51.8 wt parts of ethylene glycol, 20 wt parts of diethylene glycol, 0.069 wt parts of calcium acetate were mixed, and

ester-exchange reaction was performed while removing the methanol at 140 - 22°C under the nitrogen gas flow. Then, 0.05 wt parts of trimethyl phosphoric acid and a polymerization catalyst (0.04 wt parts of antimony trioxide and 13.9 wt parts of adipic acid) were added and esterificated at 200 - 230°C by removing the approximate theoretical amount of water.

Next, after the pressure in the system was reduced, and the temperature was increased to reach the final condition of 280°C and 0.2 mmHg, polymerization was performed for 3 hours.

When the obtained rough composition of the polyester copolymer was analyzed, the phosphorus content ratio was 90 ppm; acid substances were 40 mol% of terephthalic acid, 33 mol% of isophthalic acid, 20 mol% of adipic acid, and 7 mol% of 5-sodium sulfo isophthalic acid; and glycol substances were 40 mol% of diethylene glycol and 60 mol% of ethylene glycol. The maximum viscosity was 0.72 (see the experiment No. 1 in Table 1). 50 g of this polyester /276 copolymer were dissolved in 95°C hot water for 40 minutes. As a result, a slightly whitish 5% aqueous solution was obtained.

On the other hand, this obtained polyester copolymer aqueous solution was coated over a 50 μ thick biaxially extended polyethylene terephthalate film and dried under a 180°C hot plate for 2 minutes. Then, after a 4% polyvinyl alcohol aqueous solution (saponification ratio = 99%) was provided over the coated surface, the surface was dried at 120°C for 3 minutes.

After an adhesive tape was adhered to the polyvinyl alcohol surface of the laminate film obtained in this manner, the peeling strength in the direction of 180° was examined. As a result, peeling did not occur to any of the polyethylene terephthalate, polyester copolymer, or polyvinyl alcohol layers. Therefore, the prepared laminate was found to have extremely strong adhesiveness.

By changing the kinds of saturated straight-chain aliphatic dicarboxylic acid, mol ratio of the saturated straight-chain aliphatic dicarboxylic acid to the aromatic dicarboxylic acid, amount of 5-sodium sulfo isophthalic acid dimethyl, and diethylene glycol amount, the ester-exchange process was performed using the same technique. Polymerized polyester shown in experiment No. 2 - 20 were obtained after a coloring prevention agent and polymerization catalyst were added to the obtained reaction material.

Table 1 shows the composition ratios of respective copolymerized polyesters and evaluation results.

Table 1 (first 6 columns)

No.	組成分()内 名 数				分子量
	炭素	水素	酸素	窒素	
1	アクリル酸 (40/60)	アクリル酸 (20)	アクリル酸 (11)	(40)	アクリル酸 (60)
2	" (40/60)	アクリル酸 (20)	" (7)	(40)	" (60)
3	" (40/60)	アクリル酸 (20)	" (7)	(40)	" (60)
4	" (40/60)	アクリル酸 (20)	" (7)	(40)	" (60)
5	アクリル酸 (64)	アクリル酸 (7)	" (7)	(40)	" (60)
6	" (64)	" (10)	" (7)	(40)	" (60)
7	" (73)	" (20)	" (7)	(40)	" (60)
8	" (64)	" (17)	" (7)	(40)	" (60)
9	" (51)	" (42)	" (7)	(40)	" (60)
10	アクリル酸 (73)	" (22)	" (8)	(40)	" (60)
11	" (40/60)	" (20)	" (4)	(40)	" (60)
12	" (40/60)	" (20)	" (9)	(40)	" (60)
13	" (40/60)	" (20)	" (15)	(40)	" (60)
14	" (40/60)	" (22)	" (7)	(28)	" (78)
15	" (40/60)	" (20)	" (7)	(38)	" (49)
16	" (40/60)	" (20)	" (7)	(40)	" (60)
17	" (40/60)	" (20)	" (7)	(78)	" (10)
18	" (40/60)	" (20)	" (7)	(40)	" (60)
19	" (40/60)	" (20)	" (7)	(40)	" (60)
20	アクリル酸 (70)	" (20)	" (7)	(40)	" (60)

Key for Table 1 (first 6 columns):

Experiment No.	Acid component (mol%)			Glycol component (mol%)	
	Aromatic dicarboxylic acid	Saturated straight chain aliphatic dicarboxylic acid	ester-forming sulfonic acid alkali metallic salt	Diethylene glycol	Other glycol
1	Terephthalic acid/isophthalic acid	Adipic acid	5-sodium sulfo isophthalic acid		Ethylene glycol
2	Succinct acid	Succinic acid			
3		Gluthalic acid			
4		Nona methylene dicarboxylic acid			
5	Terephthalic acid	Adipic acid			
6					
7					
8					
9					
10	Terephthalic/isophthalic acid				
11					
12					
13					
14					
15					
16					
17					
18					1,4-butene diol/ethylene glycol (20/40)
19					1,6-hexane diol/ethylene glycol (20/40)
20	2,6-naphthalene dicarboxylic acid				Ethylene glycol

Table 1 (middle 2 columns)

Phosphorus amount in polymer	Maximum viscosity
90	0.720
95	0.649
92	0.712
85	0.695
100	0.607
95	0.728
94	0.754
96	0.710
85	0.722
79	0.775
80	0.759
95	0.713
89	0.699
89	0.701
98	0.765
96	0.752
95	0.744
95	0.728
87	0.695
91	0.681

Key for Table 1 (middle 2 columns)

Phosphorus amount in polymer	Maximum viscosity

Table 1 (right 7 columns

水 場 性	トイロ・フナ グアイア池		イサナ 池	イサナ 池	イサナ 池	耐水性	均一散布性
	20時間	1ヶ月後	1ヶ月後	1ヶ月後	1ヶ月後		
わずかに白濁される	5	5	8	4	4		極めて良好
不透明物が認められる 場合あり	2	—	2	8	4		やや劣る
〃	2	—	2	8	4		〃
白濁はあるが良好	5	2	2	4	4		良 好
多量の不透明物を認め る	1	—	—	4	4		最も不良あり
若干の不透明物が認め られるが良好	4	4	4	4	4		良 好
白濁はあるが良好	5	5	5	4	4		〃
〃	5	5	4	4	4		〃
〃	4	4	4	4	2		〃
多量に不透明物が出 る	—	—	—	—	—		最も不良あり
白濁はあるが良好	4	4	4	4	4		良 好
〃	4	4	4	4	2		極めて良好
わずかに白濁される	5	5	5	4	1		〃
若干の不透明物が認め られる 場合あり	2	2	2	8	4		やや劣る
若干の白濁がある が良好	5	5	5	4	4		良 好
〃	5	5	5	5	4		〃
〃	5	5	8	4	4		〃
わずかに白濁される	5	5	5	5	4		極めて良好
〃	5	5	5	5	4		〃
白濁はあるが良好	5	5	5	4	4		良 好

Key for Table 1 (first 7 columns)

Water solubility	Adhesiveness to polyvinyl alcohol		Adhesiveness to gelatin (1 month later)	Adhesiveness to polyester film	Water resistance	Application uniformity
	After 24 hours	After 1 month				
Slightly whitish						Extremely excellent
Insoluble substance was recognized and slightly inferior						Slightly inferior
Whitish but excellent						Satisfactory
A large amount of insolubles						Uneven coating
Small amount of insoluble but excellent						Satisfactory
Whitish but excellent						
Uniform coating property						Uneven coating
Whitish but excellent						Satisfactory
						Extremely excellent
Slightly whitish, excellent						
Small amount of insolubles, slightly inferior						Slightly inferior
Slightly whitish, excellent						Satisfactory
Slightly whitish, excellent						Extremely excellent
Whitish, excellent						Satisfactory

Experiment No. 2 - 5, 9, 10, 12 - 14 were the comparison tests conducted outside of the ranges of this invention.

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In the Experiments 2 - 4, succinic acid, glutthalic acid, and nona methylene dicarboxylic acid were used as the straight-chain dicarboxylic acid. In the case of succinic acid and glutthalic acid, adhesiveness to the polyvinyl alcohol and gelatin was completely absent. Also, in the case of nona methylene dicarboxylic acid, the adhesiveness was worsened with the passage of time. Therefore, to obtain the aimed adhesive strength, 4 - 8 of methylene groups were found suitable.

As shown in the Experiment 1, by combining at least two kinds of aromatic dicarboxylic acid substances, further improved results could be obtained on the coating uniformity and water solubility.

With the Experiments 5 - 9, the relation between the mol ratio of saturated straight-chain aliphatic dicarboxylic acid and aromatic dicarboxylic acid were shown. When the mol ratio was small, the water solubility, coating uniformity, and adhesiveness were insufficient, while the increased ratio caused insufficient water-resistance. Therefore, to satisfy these characteristics, the mol ratio of aromatic dicarboxylic acid component and aliphatic dicarboxylic acid should be 10/1 - 10/7.5.

Experiments 10 - 13 are examples for improving the water-solubility and adhesive effectiveness by copolymerizing the ester-forming sulfonic acid alkali metallic salt compounds. These effects are produced by adding ester-forming sulfonic acid alkali metallic salt for an amount of 3.5 - 8 mol% per the amount of acid component.

If the amount is less than 3.5 mol%, as shown in the table, the water-solubility cannot be sufficiently improved, whereas an amount exceeding 8 mol% results in inferior water-resistance when used practically.

Experiments 14 - 17 show the effects based on the diethylene glycol amount of the glycol component. When the amount of diethylene glycol is high, water-solubility and adhesiveness to polyvinyl alcohol and gelatin deteriorate. As shown, no effect is provided unless the amount exceeds 50 mol%.

Moreover, as shown in the Experiments 18 and 19, when at least two kinds of glycols other than diethylene glycol are combined, more preferable results can be obtained.

Experiment 20 is an example when aromatic dicarboxylic acid is in the place of terephthalic acid and isophthalic acid.

In addition, experiments conducted for further clarifying the effect of phosphorus compound. The results are shown in Table 2.

Table 2 (first 7 columns)

試 料 名	炭 水 化 物 () 内 容			グリコール成分 () 内 容		リン化合物
	芳香族 ジカルボン酸	飽和直鎖状 ジカルボン酸	エステル類 アルカリ金属塩	ジエチレン グリコール	他の グリコール	
21	テレフタル酸/イソフタル酸 (48/33)	アジピン酸(20)	5-ナトリウムスルホイソフタル酸 (7)	(40)	エチレン グリコール (40)	—
22	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	リン酸トリノール
23	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	“
24	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	“
25	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	“
26	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	“
27	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	“
28	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	ジノナフタレート ビスホスフェート
29	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	リン酸ホウ素
30	“ (40/33)	“ (20)	“ (7)	(40)	“ (40)	“
31	“ (40/33)	“ (20)	“ (7)	(40)	1,6-ヘキサジ ンジオール (20/20)	星 リ ン 酸

Key for Table 2 (first 7 columns)

Experiment No.	Acid component (mol%)			Glycol component (mol%)		Phosphorus compound
	Aromatic dicarboxylic acid	Saturated straight chain aliphatic dicarboxylic acid	Ester-forming sulfonic acid alkali metallic salt	Diethylene glycol	Other glycol	
21	Terephthalic acid/isophthalic acid	Adipic acid	5-sodium sulfo isophthalic acid		Ethylene glycol	
22						Phosphoric acid trimethyl
23						
24						
25						
26						
27						
28						Dimethyl phenyl propionate
29						Phosphoric acid boron
30						
31					1,6-hexane diol/ethylene glycol (20/40)	Phosphorous acid

Table 2 (continued)

重合体 中のリン量 (PPD)	水 溶 性	ポリビニルアルコール に対する接着性		ポリエス テルフィ ルムへの 接着性	耐水性
		24時間後	1ヶ月後		
0	わずかに白濁良好	5	3	4	2
18	"	5	3	4	3
23	"	5	5	4	4
156	わずかに白濁優れる	5	5	4	4
735	"	5	5	4	4
928	白濁はあるが良好	5	4	4	4
1105	"	4	3	2	2
96	わずかに白濁優れる	5	5	4	4
87	"	5	5	4	4
135	"	5	5	4	4
241	白濁はあるが良好	5	5	4	4

Key:

Phosphorus amount in polymer	Water solubility	Adhesiveness to polyvinyl alcohol		Adhesiveness to polyester film	Water resistance
		After 24 hours	After 1 month		
	Whitish, satisfactory				
	Whitish, satisfactory				
	Whitish, excellent				
	Whitish, satisfactory				
	Whitish, excellent				

As shown with the experiments 21 and 22, if the amount of phosphorus in the polyester copolymer is less than 20 ppm, water resistance and adhesiveness to polyvinyl alcohol deteriorate with the passage of time worsen. On the other hand, as shown with the experiment 27, an amount exceeding 1000 ppm is not preferable, as it cause the deterioration of adhesiveness to a polyester film and water resistance. As shown in the table, the preferred range is 20 - 1000 ppm.

Operational example 2:

33.2 wt parts of terephthalic acid, 29.0 wt parts of isophthalic acid, and 27.9 wt parts of ethylene glycol were put in a reaction can and esterificated at 220 - 245°C under increased pressure. Then, 19 wt parts of diethylene glycol, 9.5 wt parts of 5-sulfo isophthalic acid potassium styrene glycol ester, 29 wt parts of sebacic acid ethylene glycol ester, 0.06 wt parts of phosphoric acid as a phosphorus compound, and 0.035 wt parts of tri antimony oxide as a polymerization catalyst were mixed. Next, after the pressure in the system was reduced, and the temperature was increased to reach the final condition of 280°C and 0.2 mmHg, polymerization was performed for 3 hours.

The rough composition of the copolymer obtained in this manner consisted of 40 mol% of terephthalic acid, 35 mol% of isophthalic acid, 20 mol% of sebacic acid, and 5 mol% of 5-potassium sulfo isophthalic acid, and as the glycol substances, 40 mol% of diethylene

glycol and 60 mol% of ethylene glycol. The maximum viscosity was 0.59

This polymer, in the melted state, was added in 95°C hot water and dissolved under stirring for 35 minutes.

This solution was gradually cooled to the room temperature. As a result, although slightly whitish, the obtained material was a 7.5% aqueous solution of uniform concentration.

This aqueous solution was coated over a 12 μ thick polyethylene terephthalate film.

(1) Two films were laminated on their coated surfaces, pressed using a 140°C iron, and peeled to examine the adhesiveness. As a result, the base film was torn due to extremely strong adhesiveness.

(2) After a 3% polyvinyl alcohol aqueous solution was coated over the coating surface, the peeling test was conducted using an adhesive tape. As a result, the polyvinyl alcohol layer did not peel at all. Moreover, after the films were left untouched for 1 month in the atmosphere of 40°C and 65% RH, the same adhesive strength was obtained.